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ANALYSIS OF FLUORINE GAS BY REACTION WITH MERCURY

By Robert E. Seaver

Lewis Research Center
Cleveland, Ohio

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SUMMARY

In this investigation the analysis of fluorine gas by reaction with mercury at room temperature was studied and compared with the analysis by reaction with refluxing mercury. The results indicate that analysis with hot mercury in a glass system may yield erroneous data because of the formation of silicon tetrafluoride. The cold-mercury method appears to be a reliable method for the routine analysis of commercially pure fluorine gas for elemental fluorine content. The cold-mercury method may be coupled with infrared analysis or other analytical techniques to give a complete analysis of fluorine gas.

INTRODUCTION

Several methods have been presented in the literature for the analysis of fluorine-containing gases. Among these, the two best methods appear to be the sodium chloride method and the mercury method. The sodium chloride method (ref. 1) consists in reacting fluorine with sodium chloride and then analyzing the ensuing gases. This method is tedious and time consuming. In the mercury method, fluorine is reacted with either hot (ref. 2) or cold (ref. 3) mercury, and in some cases the residual gases may be analyzed. Analysis of the residual gases is difficult, since these gases are generally present in small quantities.

In several of the analyses carried out at the Lewis Research Center with the hot-mercury method, unexpectedly low results were obtained for the purity of fluorine gas (specified 98 percent minimum purity by manufacturer). An investigation was therefore undertaken to determine the suitability of the hot-mercury method for analysis of fluorine gas and to compare the hot- and cold-mercury methods. The results of this study are reported herein.

APPARATUS

The glass vacuum system used in the analyses with mercury is illustrated in figure 1. The system consisted essentially of a reaction flask, a manometer, a measuring bulb, a trap for condensing fluorine with liquid nitrogen, and a soda-lime reactor for disposing of the fluorine.

Two types of reaction flasks were used in the analyses. Reaction flask A, used with cold mercury, was a 500-cubic-centimeter glass bulb that contained a glass-enclosed magnetic stirring bar and was connected to a mercury reservoir. Reaction flask B, used with hot mercury, was a 500-cubic-centimeter glass bulb enclosed in a heating mantle and connected to a water-cooled reflux condenser.

Prior to use, all glassware was pretreated with fluorine for at least 16 hours. A layer of fluorocarbon oil was used to protect the mercury in the manometer. The various volumes of the system were known to within 0.5 percent. All calculations involved in the analyses were based on the ideal gas law.

For the infrared analyses a 5.2-centimeter monel gas cell was used. The cell was equipped with sodium chloride (NaCl) windows that had been coated with a layer of sodium fluorosilicate (Na_2SiF_6) because of the reaction of NaCl with silicon tetrafluoride (SiF_4) in previous analyses. The Na_2SiF_6 absorbs at about 14 microns and does not interfere with other absorbtion peaks present in an analysis.

PROCEDURE

In the hot-mercury method, fluorine gas was placed in the measuring bulb and the amount of gas was determined. The fluorine was then allowed to expand into reaction flask B, which contained about 25 cubic centimeters of refluxing mercury. The stopcock to the flask was closed, and, after the amount of gas remaining in the rest of the system was determined, the system was evacuated. The mercury was refluxed for about $1\frac{1}{2}$ hours, and the amount of residue gas in the flask was then measured.

In the cold-mercury method, fluorine gas was placed directly in reaction flask A, and the amount of gas was determined. The flask was then closed off, and about 6 cubic centimeters of mercury were added. The mercury was then agitated at room temperature by the magnetic stirrer. As the reaction took place, a coating of mercury fluoride formed on the surface of the mercury. The agitation constantly replaced this coating with fresh mercury at the surface. When the fluorine had all reacted, as indicated by failure of the mercury fluoride to form on the fresh mercury, the amount of gas remaining in the bulb was determined.

In both methods, the fluorine was either taken directly from the supply cylinder or from the vapor over liquid fluorine, which was condensed in a liquid-nitrogen bath. The bath was used to remove condensable impurities, including SiF_4 and presumably hydrogen fluoride (HF).

A procedure identical with that of the cold-mercury method was used for checking the reaction of oxygen and oxygen-fluorine mixtures with mercury, except that the liquid-nitrogen trap was not used. For the mixtures, oxygen was added to the reaction flask first, then the fluorine was added and 30 minutes were allowed for mixing. The flask was then closed off and the mercury was added.

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DISCUSSION OF RESULTS

From the analytical data given in table I, it is apparent that the cold-mercury method gave consistently higher values for the percentage of fluorine present (percentage of gas reacted) than the hot-mercury method. Analysis of the vapor over the condensed gas from cylinder 1 indicated a fluorine content of 75.4 percent by the hot-mercury method; but, when the cold-mercury method was used, a value greater than 99 percent fluorine was obtained. The residue of the gas from the reaction with hot mercury was analyzed with a mass spectrometer and found to contain carbon tetrafluoride (CF_4), silicon tetrafluoride, oxygen, nitrogen, and argon. Quantitative infrared analysis of the residue gas showed 1.1 percent CF_4 and over 80 percent SiF_4. Since this sample had been taken from the vapor over liquid fluorine at -195.8° C, the large amount of SiF_4 was apparently due to reaction with the hot glass.

Oxygen gas did not appear to react with mercury under the conditions of the cold-mercury method, either alone or mixed with fluorine. When oxygen alone was placed in contact with cold mercury, there was no change in pressure after 4 hours. When a mixture of 96.41 percent fluorine from cylinder 1 and 3.59 percent oxygen was reacted with cold mercury, 4.53 percent of the gas remained unreacted. Subtraction of the unreactive gas in the fluorine from this value leaves 3.60 percent oxygen, which compares well with the percentage of oxygen in the original mixture.

Infrared analyses of fluorine gas taken directly from the cylinders are given in table II. The percentages given for oxygen bifluoride (OF_2) are maximum limits because OF_2 has a comparatively weak absorption in the infrared spectrum.

No attempt was made to determine the HF content of the gas; however, this may be accomplished by determining the amount of condensables in the gas or by use of sodium fluoride (ref. 1).

CONCLUSION

The cold-mercury method appears to be a reliable method for the routine analysis of fluorine gas for total fluorine content, whereas the hot-mercury method may give erratic results because of the formation of silicon tetrafluoride. Oxygen, which may be a contaminant in fluorine gas, does not react with cold mercury under the conditions of the analysis described. The cold-mercury method, coupled with infrared analysis or other analytical techniques, may be used to give a complete analysis of fluorine gas.

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TABLE I. - SUMMARY OF FLUORINE ANALYSES

Supply cylinder	Hot-mercury method	Cold-mercury method
	Fluorine, mole percent	
Cylinder gas		
1	84.9	99.0
2	[a]78.0	97.2
3	[a]80.0	98.7
Vapor from condensed gas		
1	75.4	99.2
1	----	99.2
4	----	98.4

[a]Data obtained by other investigators at the Lewis Research Center.

TABLE II. - INFRARED ANALYSIS OF CYLINDER GASES

Supply cylinder	Constituent, mole percent			
	CF_4	SiF_4	C_2F_6	OF_2
1	0.02	0.03	<0.01	<0.07
4	1.37	.07	.06	<.07

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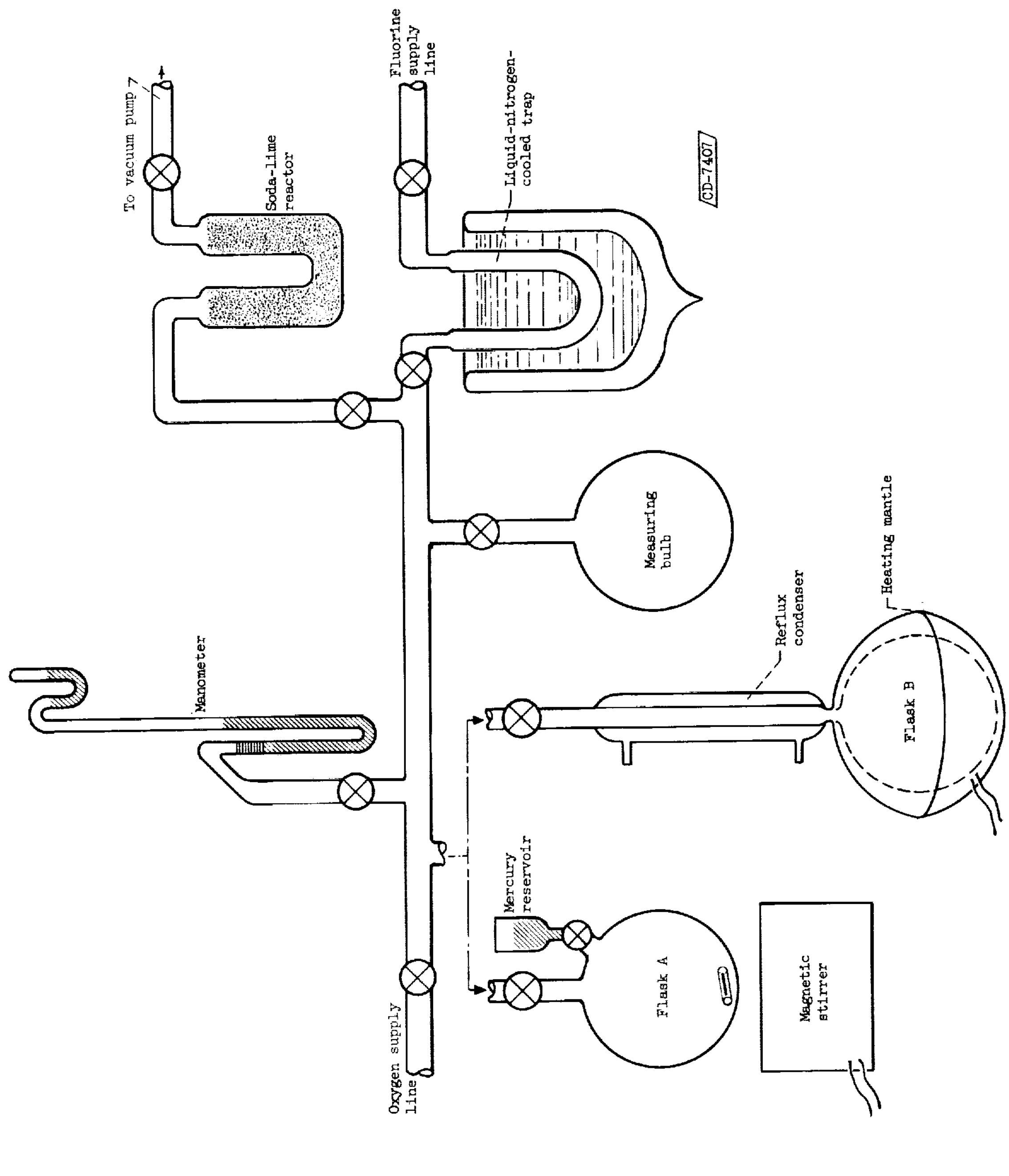

Figure 1. - Fluorine analysis system.